

SCIENCE FOR GLASS PRODUCTION

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EQUILIBRIUM OF OXIDE FORMS OF COPPER IN COLORED OPTICAL GLASSES

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The formation of the equilibrium $\text{Cu(I)} \leftrightarrow \text{Cu(II)}$ in colored optical glasses under the combined action of several factors is examined. It is shown that the oxidation of copper intensifies with increasing total copper content by weight, increasing content of carbonates in the mix, and increasing basicity of the matrix and depends primarily on the ratio of chromium, arsenic, and copper oxides. A factor is proposed for making a quantitative assessment of the combined effect of the chromium and arsenic oxides on the copper equilibrium.

Key words: optical glass, color, copper valence.

Colored optical glass is used in instrument building to produce color filters that regulate light transmission in the visible and nearby IR and UV regions of the spectrum. To obtain the required spectral characteristics copper oxide is introduced into the mix for blue (BG), blue-green (BGG), and violet (VG) glasses and copper oxide together with chromium oxide is introduced into green (GG) and yellow-green (YGG) glasses (OST 3-4375-79). Up to 0.1% As_2O_3 (molar content) is introduced into individual compositions in order to correct the optical and operational properties.

The following expression is used to evaluate the specific index of absorption χ_λ of a coloring element in glass in order to make a quantitative evaluation of the intensity of absorption by the element:

$$\chi_{\lambda, \text{Fe}} = \frac{-\log \tau_\lambda - 2D_{\text{pm}}}{l m_{\text{Fe(total)}}},$$

where τ_λ is the light-transmission of the glass sample, fractions of unity; D_{pm} is a correction for reflection, calculated according to the relation [1] $D_{\text{pm}} = -2\log(1 - r)$; l is the thickness of the sample, cm; and, $m_{\text{Me(total)}}$ is the content

by weight of the coloring element in the glass in terms of metal, %.

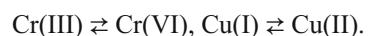
The scattering index r is related with the index of refraction n of the glass by the expression [1]

$$r = \frac{(n-1)^2}{(n+1)^2}.$$

Copper and chromium are d elements. In silicate glasses each element coexists in two valence forms: Cu(I), Cu(II) and Cr(III), Cr(VI). Their spectral curves of the specific absorption index χ_λ are presented in Fig. 1 [2]. Univalent copper has no absorption bands in the visible and closest adjoining regions of the spectrum, and Cu(II) forms two complexes with oxygen — a quadruply coordinated “yellow” complex absorbs in the short-wavelength region and a “blue” complex $[\text{Cu(II)}\text{O}_6]$ possesses an intense band at 750–800 nm.

Hexavalent chromium intercepts radiation in the blue part of the spectrum, while tetravalent chromium has two strong bands in the visible region near 460–480 and 660–680 nm.

It is evident that the spectral curve and the light transmission of glass colored with copper or with a combination of copper and chromium will depend considerably on the ratio of the oxide forms of these elements, i.e., on the equilibrium



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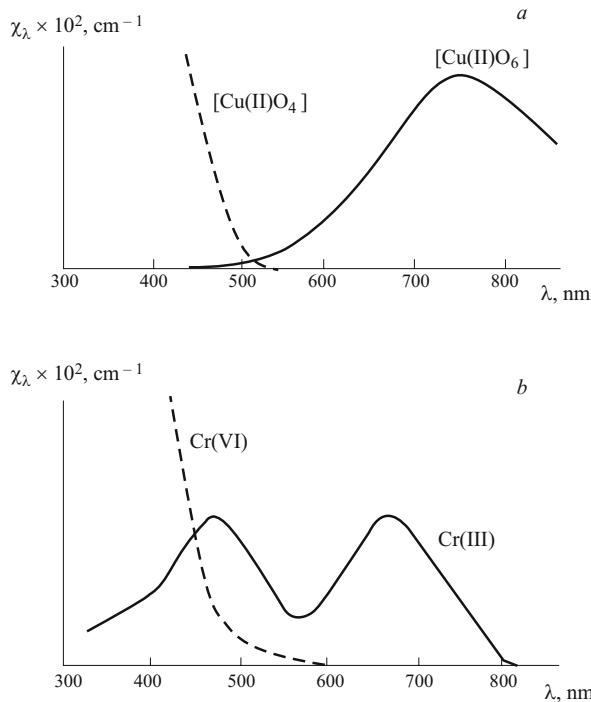


Fig. 1. Spectral curves of the specific absorption indices χ_λ of copper (a) and chromium (b) in silicate glasses.

The equilibrium between the oxidized and reduced forms of the d elements has been studied in greatest detail for the iron impurity most often encountered in glass and depends on the set of parameters of the technological process: amount of d element, acid – base properties of the glass matrix, oxidation – reduction and temperature – time conditions of glass making and production, the anionic composition of the raw materials for introducing alkali and alkali-earth components into the mix, and the presence and concentration of other heterovalent elements [3].

In our work we have examined the formation of copper equilibrium in commercial colored optical glasses as a function of the copper concentration, the acidity – basicity of the matrix, the anionic composition of the mix, the presence of other heterovalent elements — chromium and arsenic.

In glasses containing iron oxide as an impurity, a decrease of its concentration intensifies reduction, increasing the Fe(II) fraction [4]. For copper, this dependence has not been studied for all practical purposes.

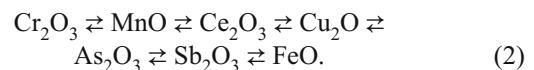
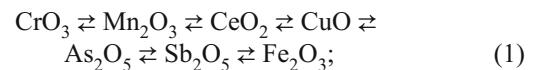
It is known that as the concentration of the basic oxides in glass increases and the content of acidic oxides decreases, the coloring heterovalent elements strive to increase the degree of oxidation and vice versa. For quantitative assessment of the acid – base properties of matrices we use the basicity [5] calculated according to the expression

$$K_{\text{bas}} = \frac{4.6\text{Al}_2\text{O}_3 + 4.7(\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{BaO} + 0.3\text{ZnO} + 0.7\text{CaO} + 0.7\text{PbO} - \text{Al}_2\text{O}_3)}{0.82\text{SiO}_2 + [\text{B}_2\text{O}_3 - (\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{BaO} + 0.3\text{ZnO} + 0.7\text{CaO} + 0.7\text{PbO} - \text{Al}_2\text{O}_3)]},$$

where SiO_2 , B_2O_3 , Al_2O_3 , K_2O , Me_2O , MeO , and so on are, respectively, the molar content of silicon, boron, aluminum, alkali- and divalent metal oxides, %.

The oxidation-reduction state of the heterovalent elements depends strongly on the form of the raw materials used for preparing the charge. According to the results of our investigations carbonates and boric acid shift the equilibrium of the most common impurity found in glass — iron — $\text{Fe}(\text{II}) \leftrightarrow \text{Fe}(\text{III})$ leftward, while nitrates act in the opposite direction.

When several heterovalent elements are present in glass simultaneously they affect one another according to the oxidation – reduction series [2]:



Each oxide on the left-hand side in a higher valence state is capable of oxidizing an oxide located on the right-hand side in a state of lower valence.

Evidently, chromium has an oxidizing and arsenic a reducing effect on copper, converting it into the forms $\text{Cu}(\text{II})$ and $\text{Cu}(\text{I})$, respectively. For quantitative assessment of the effectiveness of the influence of these elements when present simultaneously, the concept of “reduced content” γ calculated according to the expression

$$\gamma_{\text{Cr-As}} = \frac{C_{\text{Cr}} - C_{\text{As}}}{C_{\text{Cu}}},$$

where C_{Cr} , C_{As} , and C_{Cu} are the content by weight of chromium, arsenic, and copper in the glass according to synthesis converted to metal, %.

Physically, the value of $\gamma_{\text{Cr-As}}$ is the content of heterovalent elements located to left and right of copper in the oxidation-reduction series (2), referred to 1 wt.% Cu. Therefore the value of this quantity is a criterion of the oxidizing action on copper of chromium and arsenic oxides when both are present simultaneously in the glass.

If only a single heterovalent element was present besides copper in glass, the particular values of the “reduced content” were calculated as

$$\gamma_{\text{Cr}} = \frac{C_{\text{Cr}}}{C_{\text{Cu}}}; \quad \gamma_{\text{As}} = \frac{C_{\text{As}}}{C_{\text{Cu}}}.$$

Colored copper-containing optical glasses are listed in Table 1, where some of their characteristics are also presented. The concentration of divalent copper in the form $[\text{Cu}(\text{II})\text{O}_6]$ was calculated from the spectral curve of the

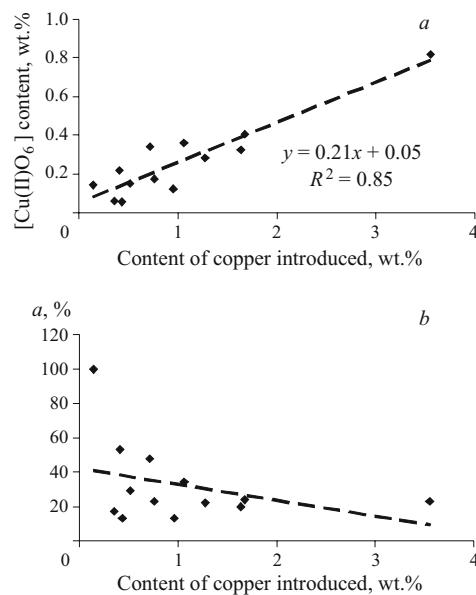


Fig. 2. $[\text{Cu(II)}\text{O}_6]$ mass content (a) and mass fraction of bivalent copper a (b) versus the total content of copper introduced into the glass.

glass by the spectrophotometric method (OST 3-728-79), based on the Bouguer – Lambert – Beer law, according to which when a definite composition of several colorants is present in the glass the absorption index α_λ of the glass for any wavelength λ is equal to the sum of the products of the individual absorption index of each ion χ_λ and its content C by weight in the glass, i.e.

$$\alpha_\lambda = \sum \chi_\lambda C.$$

For a quantitative assessment of the position of the equilibrium $\text{Cu(II)} \rightleftharpoons \text{Cu(I)}$, we calculated the mass fraction of

the divalent copper α in the compound $[\text{Cu(II)}\text{O}_6]$ relative to all of the copper introduced into the glass:

$$\alpha = \frac{C_{[\text{Cu(II)}\text{O}_6]}}{C_{\text{Cu}}} \times 100\%,$$

where $C_{[\text{Cu(II)}\text{O}_6]}$ and C_{Cu} are the mass contents of the divalent (as calculated) and total (according to synthesis) copper in reference to the metal, %.

We note that according to the data of [6] the fraction of the coordination form $[\text{Cu(II)}\text{O}_4]$ is 1 – 1.5 orders of magnitude less than that of $[\text{Cu(II)}\text{O}_6]$ in all silicate glasses except titanium-containing flints, so that the content of quadruply coordinate copper was not determined in the present work. Figure 2 shows the interrelation of the $[\text{Cu(II)}\text{O}_6]$ content and the fraction of divalent copper a with the total content of copper in the glass. The mass content of $[\text{Cu(II)}\text{O}_6]$ (y) increases proportionally with increasing content of the copper (x) introduced into the glass. The dependence can be reliably described by the linear equation

$$y = 0.21x + 0.05.$$

As for the $[\text{Cu(II)}\text{O}_6]$ fraction, the equilibrium $\text{Cu(I)} \rightleftharpoons \text{Cu(II)}$ tends to shift leftward with increasing total copper content.

As noted above, the equilibrium of the valence forms of a heterovalent element in glass is formed under many factors operating in different directions; two such factors are the acid – base properties of the matrix and the presence of other heterovalent elements in the composition.

Figure 3a shows the tendency of α to increase and the equilibrium $\text{Cu(I)} \rightleftharpoons \text{Cu(II)}$ to shift rightward as K_{bas} increases, which conforms to the classical ideas [4]. At the

TABLE 1.

Glass	K_{bas}	Content, wt.%						
		according to synthesis			computed		$\gamma_{\text{Cr-As}}$	γ_{As}
		As	Cr	Cu	α	$[\text{Cu(II)}\text{O}_6]$		
BG-1	3.14	0.227	–	0.360	17	0.061	– 0.63	0.63
BGG-17	2.58	0.227	–	0.439	13	0.057	– 0.52	0.52
BGG-7	2.53	–	–	0.767	23	0.176	–	–
VG-1	2.88	0.235	–	0.959	13	0.125	– 0.25	0.25
BG-15	2.16	0.152	–	1.278	22	0.281	– 0.12	0.12
BG-8	2.91	0.227	–	1.637	20	0.327	– 0.14	0.14
BGG-8	2.53	–	–	1.678	24	0.403	–	–
BGG-9	2.53	–	–	3.555	23	0.818	–	–
UGG-9	3.11	0.227	0.318	0.143	100	0.143	0.64	–
GG-1	2.96	0.227	0.607	0.415	53	0.220	0.92	–
UGG-1	2.96	0.227	0.753	0.519	29	0.151	1.01	–
GG-11	3.56	–	0.376	0.719	48	0.341	0.52	– 0.52
GG-3	2.47	–	0.322	1.062	34	0.361	0.30	– 0.30

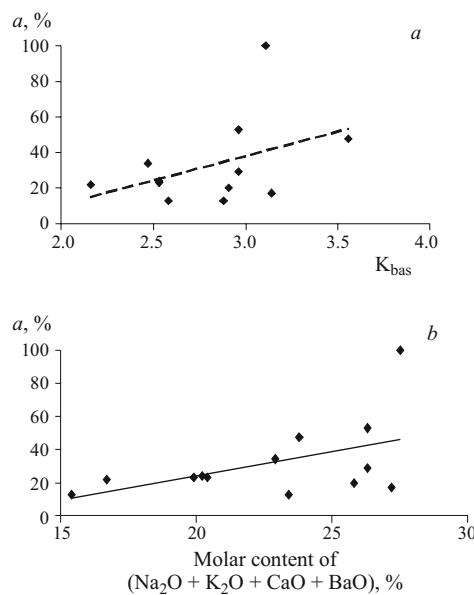


Fig. 3. Mass fraction a of bivalent copper versus the basicity of the glass (a) and the total molar content of $\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{BaO}$ (b).

same time, as K_{bas} increases, the content of uni- and bivalent oxides, introduced predominantly by carbonate salts, in the glass increases. Judging from Fig. 3b, carbonates have an oxidizing effect on copper, transferring it into a bivalent state.

In accordance with the oxidation – reduction series (2) chromium oxide should oxidize while arsenic should reduce copper, correspondingly shifting the equilibrium $\text{Cu(I)} \rightleftharpoons \text{Cu(II)}$ rightward (chromium) and leftward (arsenic). The data in Fig. 4 confirm this supposition: the fraction of bivalent copper tends to decrease proportionately as γ_{As} increases and to increase as γ_{Cr} increases. In addition, the dependence of $\alpha(x)$ on $\gamma_{\text{As}}(y)$ is reliably described by a quadratic equation:

$$y = 56.94x^2 - 48.56x + 24.02 \quad (\text{dashed curve in Fig. 4a}).$$

When chromium and arsenic oxides are present simultaneously in glass, displacing the equilibrium $\text{Cu(I)} \rightleftharpoons \text{Cu(II)}$ in

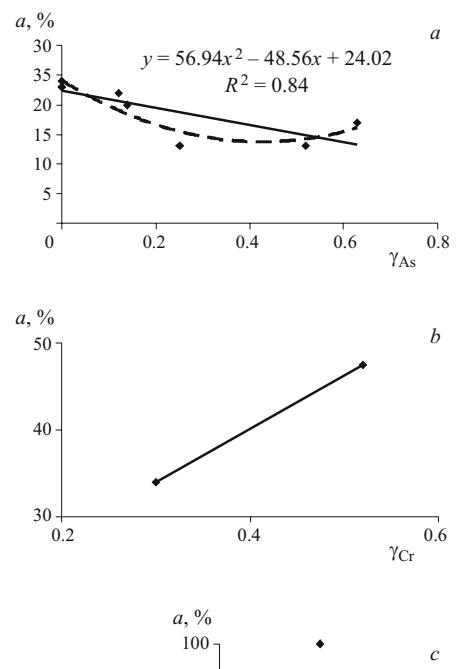


Fig. 4. Mass fraction a of bivalent copper versus the values of γ_{As} (a), γ_{Cr} (b), and $\gamma_{\text{Cr-As}}$ (c).

different directions, the oxidizing effect of this mixture is proportional to the value of $\gamma_{\text{Cr-As}}$ (see Fig. 4c), an increase of which shifts this equilibrium rightward.

In summary, the oxidation of copper in colored optical glasses intensifies as the total mass content of copper increases, as the content of carbonates in the mix increases, and as the basicity of the matrix and $\gamma_{\text{Cr-As}}$ increase.

In Table 2 the glasses studied are divided into four groups with successively increasing fraction of bivalent copper: up 20, from 21 to 30, from 31 to 50, and $> 50\%$.

TABLE 2.

Group*	K_{bas}	Content, wt.%						$\gamma_{\text{Cr-As}}$	$\Sigma(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{BaO})$, molar content, %	The group contains the glasses			
		according to synthesis			computed								
		As	Cr	Cu	α	$[\text{Cu(II)}\text{O}_6]$							
1	2.87	0.229	–	0.586	14.3	0.081	–0.47	22.0	BG-1, BGG-17, VG-1				
2	2.60	0.101	0.126	1.572	23.5	0.359	0.13	21.6	BGG-7, BGG-8, BGG-9, BG-15, BG-8, UGG-1				
3	3.02	–	0.349	0.891	40.7	0.351	0.41	23.4	GG-3, GG-11				
4	3.04	0.227	0.463	0.279	76.5	0.182	3.04	26.9	UGG-9, GG-1				

* Averages over a group of values of the indicators are presented.

The steady increase of the value of α corresponds well to an increase of $\gamma_{\text{Cr-As}}$ from the first to the fourth group. No similar clear relation is observed for the other parameters presented in Table 2. Hence it follows that the chromium and arsenic oxides have a dominant effect on the equilibrium $\text{Cu(I)} \rightleftharpoons \text{Cu(II)}$ in colored optical glasses. It is best to use the coefficient $\gamma_{\text{Cr-As}} = (C_{\text{Cr}} - C_{\text{As}})/C_{\text{cu}}$ as the criterion for their oxidizing effect on copper when they are present simultaneously.

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